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Defect-induced Modifications in Wetting Behavior on Micro-Nano-Hierarchical Textured Hydrophobic Surfaces

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Superhydrophobic surfaces, those exhibiting a static contact angle (*CA*) with water of greater than 150° and a sliding angle (*SA*) of less than 5°, have recently attracted significant attention from both researchers and practictioners.[1] This interest is motivated by the alluring water repellency properties of natural entities such as water-repellent leaves (lotus, rice, taro, etc), butterfly wings, mosquito eyes, and water strider legs. By mimicking the design of surfaces possessed by these examples, artificial superhydrophobic behavior has been demonstrated.[1] It is now widely held that the key elements of surfaces that promote superhydrophobic states, both Cassie[2] and Wenzel,[3] include chemical composition and micro-nano-hierarchical texture.

Artificial superhydrophobic surfaces are believed to hold industrial promise in the paints and coatings sector, providing high water repellency and self-cleaning capabilities to surfaces where these characteristics are beneficial. For coated surfaces, defects in which the underlying substrate composes submicron sized regions of the interface are common. The influence of such imperfections on wetting behavior has not yet been adequately examined. In this presentation, results of a wetting study are reviewed in which water droplets are placed on a micro-nano hierarchical textured surface and allowed to make contact with the

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underlying substrate through small defects. The experiments include a polymer or oligomer substrate coated with micro-nano-hierarchical textured ZnO particles treated with octadecanethiol (ODT) to produce a hydrophobic monolayer. The ZnO particles were generated and textured by reacting zinc powder (5 wt%) for 24 hours with 30 wt% H_2O_2 adjusted to a pH of approximately 3 using formic acid.[4] Particles are isolated via filtration and residual chemicals removed through rinsing with DI water. Generated ZnO powder is then immersed for 24 hours in a 1 mM solution ODT in ethanol to hydrophobize.[5] The modified powder was then characterized by X-ray photoelectron spectra (XPS) to confirm the presence of an ODT monolayer.

For defect-free coatings, *CAs* are greater than 160° and *SAs* are less than 5°. These observations are consistent with superhydrophobic wetting described by the Cassie model, for which the liquid droplets are suspended on the ODT treated ZnO particles. They are presented to demonstrate that when completely covered by micro-nano-hierarchical textured hydrophobic ZnO particles, the nature of the underlying substrate has no influence on the observed wetting. Interesting aspects of these coatings are revealed when thin coating layers are applied. Scanning electron micrographs of substrates prepared in this manner show coverage with ZnO particles of approximately 95%, leaving about 5% of the substrate exposed. Figure 1 shows sessile drop images and lists angles for water droplets placed on these surfaces. Contact angles indicative of superhydrophobic behavior were observed for both ZnO-coated PDMS and paraffin wax substrates, $CA_{ZnO/PDMS} = 160.8 \pm 1.4°$ and $CA_{ZnO/wax} = 160.6 \pm 1.5°$, respectively. Droplets on these surfaces demonstrate high adhesion to the point that they are retained even when surfaces are inverted. This behavior is consistent with the Wenzel model, indicating that the liquid is contacting not only the ODT-treated ZnO particles but also the underlying substrate. In stark contrast, water completely wets coated glass and PET substrates, i.e., $CA_{ZnO/glass} = CA_{ZnO/PET} = 0°$, indicative of superhydrophilic behavior. Thus it would appear that the nature of the substrate is important to determining wetting under these circumstances. Interestingly, water also completely wet the ZnO-coated PSA substrate ($CA_{ZnO/PSA}$= 0°), which appears to be at odds with results for the other hydrophobic substrates. Initial PSA surfaces were cast on glass and formed exceedingly smooth coatings. This was followed by studies in which the PSA films were cast on paraffin wax and PDMS. For both of these coatings, water droplets were again observed to completely wet the surfaces (i.e., $CA_{ZnO/PSA/PDMS}$= $CA_{ZnO/PSA/wax}$= 0°).

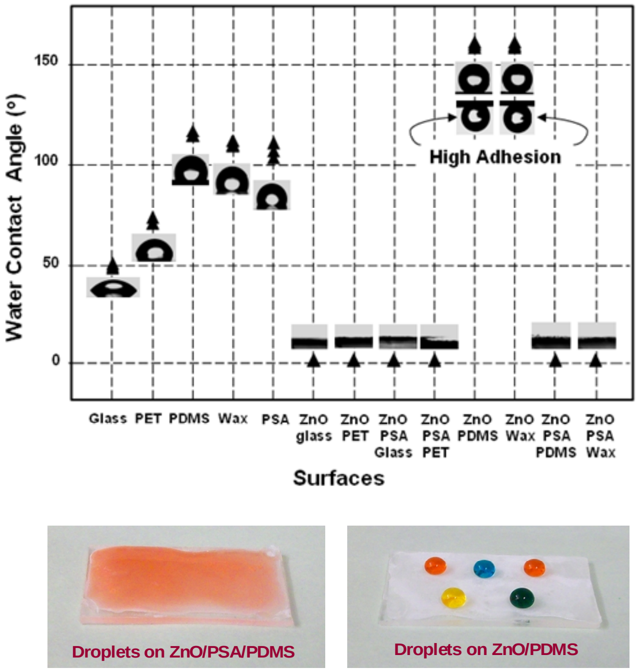

Figure 1. (Top) Water contact angles on different surfaces. Each substrate was tested three times (water droplet size: 1-10 µl). (Bottom) Photography of water droplets (mixed with ~0.1 wt% colorful ink) on mico-nano-hierarchical textured ZnO surfaces. (Left) Substrate: a PSA film on PDMS; (Right) Substrate: PDMS.

The discrepancy presented by the PSA substrate is interesting but appears to be explainable based on recent studies involving the wetting of highly viscoelastic surfaces. The CA hysteresis, i.e., *CA*(advancing) – *CA*(receding), for the PSA is large relative to other materials tested in this study, reaching almost 100°. Although the advancing *CA* is close to 107°, the high hysteresis provides evidence that the surface of the acrylic PSA is much more hydrophilic then traditional hydrophobic PDMS and wax surfaces.

In summary, our experimental results indicate that defects, which uncover the underlying substrate, can play a significant role in determining wetting behavior. Assuming that the acrylic polymer surface is at least partially wettable by water establishes a clear trend. On all defect-free coatings composed of ODT treated ZnO particles, water droplets placed on the surface demonstrates Cassie wetting and superhydrophobicity. The presence of the substrate at the interface, even at small area fractions ($\leq$5%) significantly alters wetting behavior. For hydrophilic substrates, the liquid readily moves and advances through the interface providing complete wetting even though the substrate itself may not. When this substrate is hydrophobic, the observed contact angle remains high consistent with superhydrophobicity, however the high drop adhesion to the substrate is consistent with Wenzel wetting behavior.

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